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Encapsulation of Phenolphthalein pH-Indicator into a Sol-Gel Matrix

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ABSTRACT

Transparent monolithic silica doping with phenolphthalein has been prepared via the acid-catalyzed sol-gel reactions of tetraethylorthosilicate in the presence of phenolphthalein. The immobilized phenolphthalein pH-indicator shows similar behavior as its solution counterpart. The UV/Vis spectra indicate that the phenolphthalein retains its structure during the sol-gel reactions in terms of response to pH. The phenolphthalein can be regarded as uniformly distributed in the silica matrix. This observation has been confirmed using polarized microscopy.

Key Words: Phenolphthalein pH indicator; Sol-gel encapsulation; Immobilization of indicators; Polysiloxanes

INTRODUCTION

Encapsulation of organic compounds into inorganic oxides using the sol-gel process suggests a broad range of optical materials (1–3). Chemical sensing materials were recently reported by encapsulation of analytical reagents and pH indicators (4,5). Such pH indicators were chemically or physically immobilized in a solid support (6–9). The sol-gel glasses have gained interest as matrices for chemically sensitive optical materials because of their thermal and mechanical stability, optical transparency, and shaping flexibility. There are three methods of indicator immobilization in such sol-gel glasses, including impregnation, covalent binding, and

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chemical doping. Impregnation refers to physical and chemical adsorption on the preformed glass, while chemical doping refers to incorporation of an indicator during the sol-gel reaction. In this work the chemical doping method was used for the immobilization of phenolphthalein. The immobilized phenolphthalein was prepared by doping the reagent into a sol-gel SiO_2 matrix. The synthetic procedure has been designed to obtain monolithic pieces of the doped silica. In this procedure, the alkoxide precursor (TEOS, tetraethoxysilane) is partially hydrolyzed in the presence of hydrochloric acid as catalyst. Then the appropriate concentration of phenolphthalein was added to the sol solution to obtain a monolithic polysiloxane solid material. The optimum conditions used in the preparation of immobilized phenolphthalein were examined and tested for pH measurements.

EXPERIMENTAL

Reagents and Materials

The starting materials, which include, tetraethylorthosilicate, phenolphthalein and absolute methanol were purchased from Merck, (Darmstadt, Germany) and used as received.

Spectra

The IR spectra for the immobilized phenolphthalein and free polysiloxanes were recorded on a Perkin-Elmer FT-IR Spectrometer in the range 4000–400 cm^{-1} using KBr disks. The UV/Vis spectra for immobilized phenolphthalein were recorded on a Perkin-Elmer Lambda 20 Spectrometer in the range 900–200 nm.

Polarization Optical Microscopy

The characterization of the free silica and the immobilized phenolphthalein were performed using a Ziess standard polarization microscope equipped with camera.

Preparation of Monolithic Disks

In a typical preparation of a monolithic disk (10), (20.8 g, 0.10 mol) tetraethylorthosilicate in 7 ml methanol and 3.6 ml of 0.032 M HCl were stirred for 30 minutes to obtain a homogeneous sol solution. A 21 ml of phenolphthalein solution of different concentrations of (0.005, 0.0025, 0.0015, 0.001 and 0.0005 M in methanol) was added, and stirred for 30 minutes. Portions of the solution (2.5 ml) were added into separate glass vials (10 mm in radius) covered with parafilm having fine pores and stored at room temperature. Monolithic clear gels were formed within 7 days. The monolithic materials of the entrapped phenolphthalein were left for another 7 days to obtain solid transparent crack-free disks with 0.75–0.8 mm thickness, 7 mm radius and about 0.25–0.27 g in weight. These disks were washed several times with methanol/deionized water (5×5 ml). The washes were collected in order to examine the amount of phenolphthalein leached from the monolithic disk. The experimental data are shown in Table 1. The solid monolithic disk was allowed to dry at room temperature. A monolithic polysiloxane disk free of phenolphthalein was prepared in a similar method by mixing TEOS and HCl as catalyst.

RESULTS AND DISCUSSION

Synthesis

Several samples of different concentrations of the immobilized phenolphthalein were prepared by doping the phenolphthalein into a sol-gel matrix. The synthesis was carried out by similar procedures reported (4,10) in literature including the following steps: (1) Treating TEOS with distilled H_2O and MeOH in the presence of HCl (aq, 0.032 M) at room temperature; (2) stirring the solution for 30 minutes to obtain homogeneous solution; (3) adding the appropriate concentration of phenolphthalein to the sol solution with stirring; (4) leaving the solution for several days to obtain a monolithic solid disk. The concentration

Table 1. Entrapment Capacity of Phenolphthalein by Monolithic Polysiloxane Versus Concentration

Concentration used (M)	Calcilated mg added	mg leached	mg entrapped	mg entrapped/ mg added
0.005	1.60	1.09 ± 0.03	0.51 ± 0.03	0.32
0.0025	0.80	0.52 ± 0.02	0.28 ± 0.02	0.35
0.0015	0.48	0.32 ± 0.02	0.16 ± 0.02	0.33
0.001	0.32	0.21 ± 0.03	0.11 ± 0.03	0.34
0.0005	0.16	0.11 ± 0.01	0.05 ± 0.01	0.31

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range of phenolphthalein, the catalyst concentration (0.032 M HCl), and amount of methanol added govern the monolithicity of the incorporated phenolphthalein.

Phenolphthalein Entrapment Capacity

Phenolphthalein entrapment capacity in the monolithic polysiloxane was determined by measuring the amount of phenolphthalein entrapped as a function of phenolphthalein added to initial monomer mixture. The resultant monolithic entrapped phenolphthalein disks of different concentrations of the doped material were washed with a mixture of methanol/water, 1:1 volume ratio for several times. The washes were combined, diluted to the linear phenolphthalein spectrophotometric range at 304 nm and the amount of phenolphthalein leached was calculated. The amount of phenolphthalein entrapped within the monolithic matrices was calculated by difference (Table 1). As shown in Figure 1 the amount of phenolphthalein entrapped is directly proportional to the amount of phenolphthalein added to the sol solution. The ratio of entrapped to initially added phenolphthalein seems to be constant (0.31–0.35), (Table 1) which, is also obtained from the slope of the linear curve (0.32) in Figure 1. These results imply that the number of binding sites available for phenolphthalein increase with phenolphthalein concentration. The increasing of entrapment capacity as a function of concentration is supported by similar results previously reported (10), and was confirmed from the polarized microscopy results discussed later.

UV/Vis Spectra

The electronic spectra for the free silica and the immobilized phenolphthalein were obtained in the range 900–200 nm for the acid and base forms. The results are given in Figure 2. The spectrum of the immobilized phenolphthalein (Figure 2A) exhibits no absorption bands in the Visible region and only broad band is observed at 304 nm. When the immobilized phenolphthalein monolithic disk is treated with strong base (0.10 M NaOH) solution, pink color was obtained and the spectrum is given in Figure 2B. The spectrum shows two new bands at 553 nm and 375 nm corresponding to π–π^* transitions. When the monolithic disk is treated with acidic solutions, 0.10 M HCl, the pink color disappeared gradually and the two absorption bands at 553 nm and 375 nm have almost disappeared (Figure 2C). The spectrum for the immobilized phenolphthalein treated with base is very similar to that of its counterpart in solution (Figure 2B and D). This may indicates that a very weak physical interaction between the phenolphthalein and silanol groups is evident. The change in color from colorless in acid to pink in base and vise-versa has been examined versus time. The results are given in (Figure 3A and B). From Figure 3A, there is a rapid change in the absorbance at 553 nm with time followed by slow change until it reaches its maximum. This process is reversible, as the immobilized phenolphthalein is treated with acid, the absorbance decreases and reach its minimum (Figure 3B). The reason for this behavior is that the phenolphthalein molecules adsorbed near the surface are directly affected with acid/base treatment. The plateau part may reveals that substantial portion of phenolphthalein molecules is entrapped into the bulk and the change from one form to another is reversibly and occurs due to diffusion control.

Figure 4 describes the change of the absorbance of the band at 553 nm of the immobilized phenolphthalein when treated with base (0.1 M NaOH) at different time

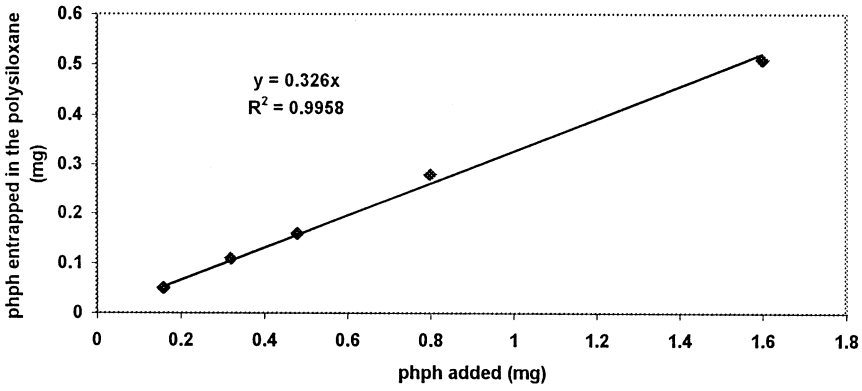

Figure 1. Entrapment of phenolphthalein in polysiloxane monolith as a function of the amount of phenolphthalein initially added to the sol monomeric mixture.

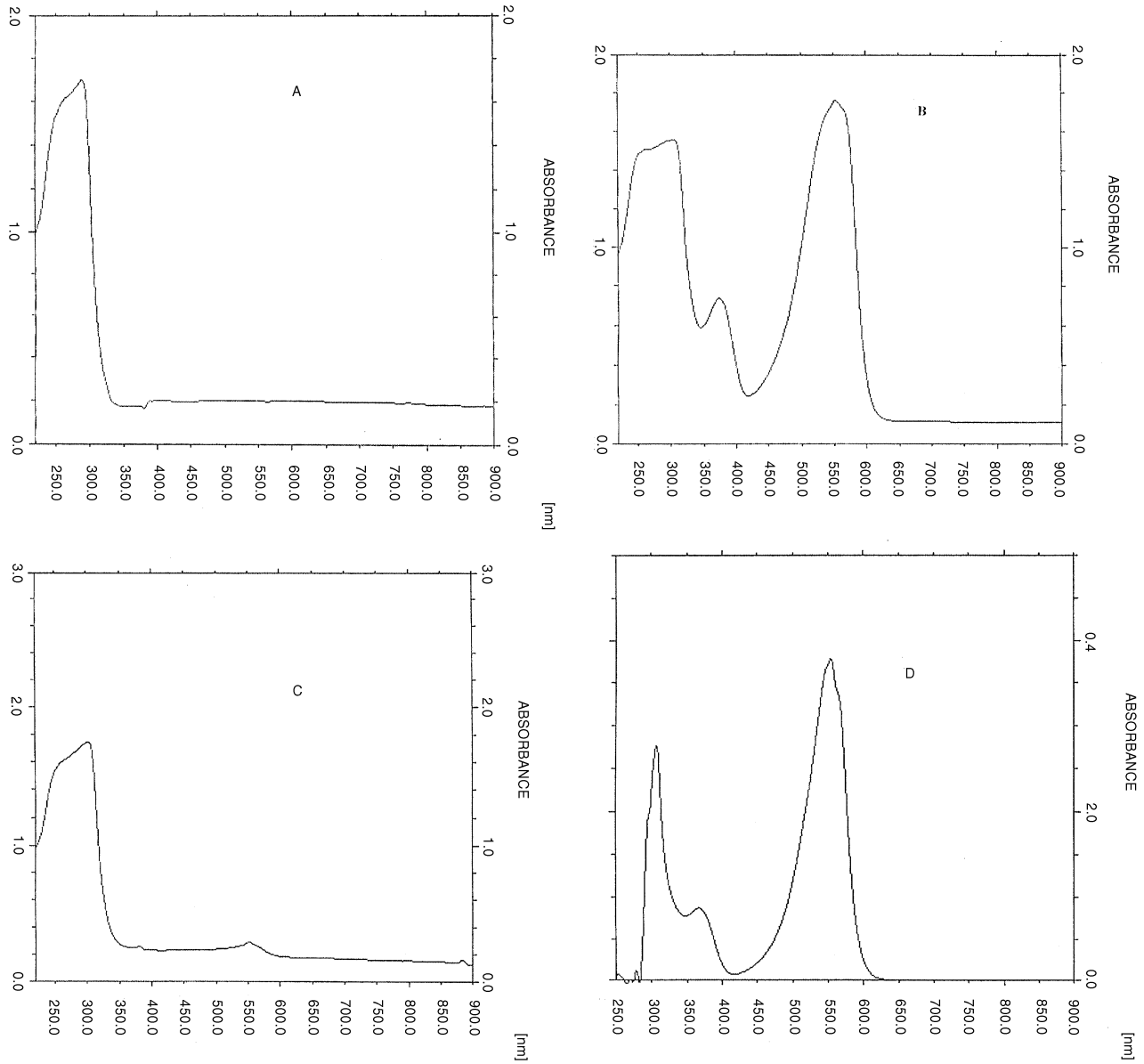

Figure 2. UV/Vis spectra of: A) immobilized phenolphthalein; B) immobilized phenolphthalein treated with aqueous 0.10 M NaOH solution; C) immobilized phenolphthalein (in b) treated with aqueous 0.10 M HCl solution; D) free phenolphthalein solution in H_2O/MeOH solvent mixture.

intervals. The absorption band reaches its maximum after nearly 50 minutes.

FT-IR Spectra

The FT-IR spectra were recorded at 4000–400 cm^{-1} for the silica free and the immobilized phenolphthalein. Figure 5 shows the FT-IR spectra of (A) silica free of phenolphthalein (B) immobilized phenolphthalein. It is possible to see the ν(Si–O–Si) symmetric and asymmetric bands located at 796 cm^{-1} and 1084 cm^{-1} respectively. The band at 955 cm^{-1} is corresponds to ν(Si–O) groups and the band in the range 3440 cm^{-1} is attributed to the presence of hydroxyl groups. These assignments are

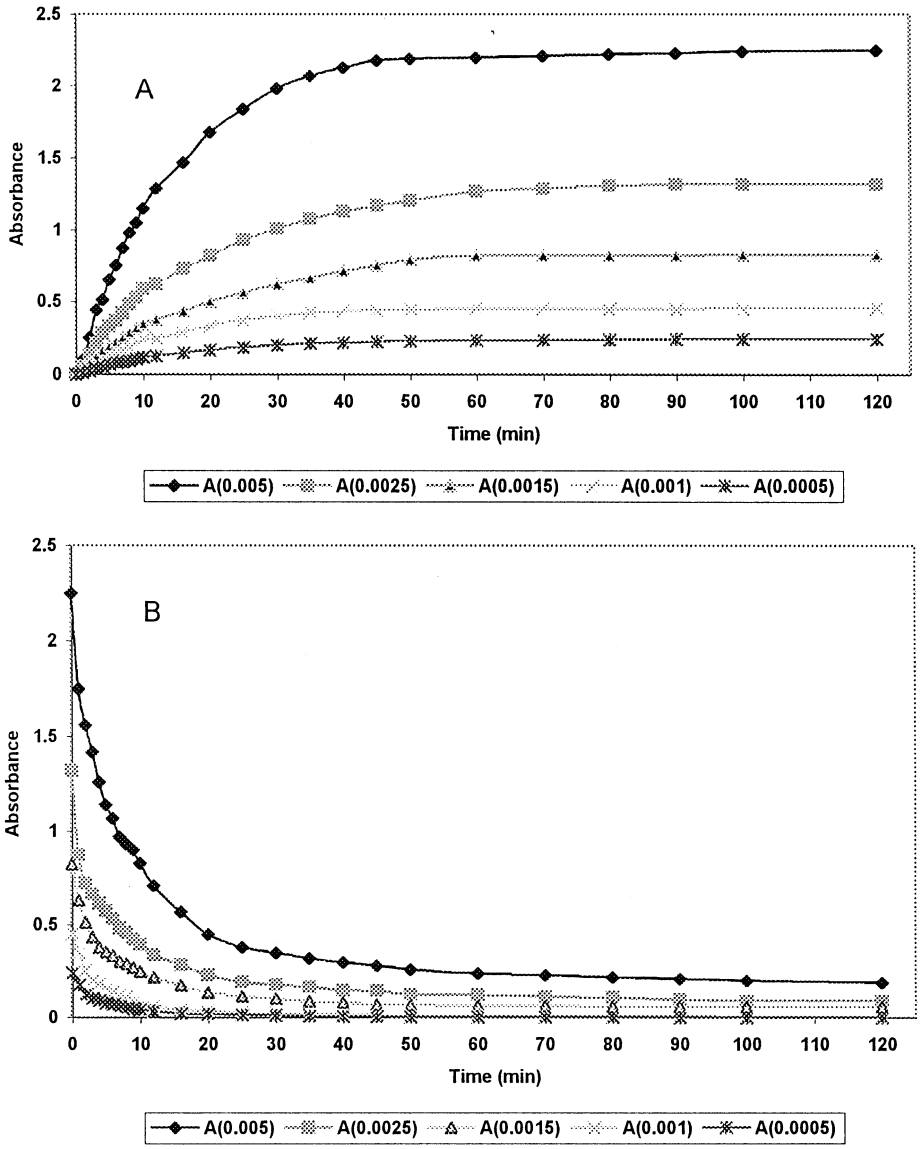

Figure 3. Absorption change of the band at 553 nm versus time, for the immobilized phenolphthalein of different concentrations upon treatment with: (A) 0.10 M sodium hydroxide solution; (B) 0.1 M HCl solution for the previous basically treated material.

based on the literature FT-IR spectra of similar systems (11–13). For the immobilized phenolphthalein, the spectrum shows a weak band at 1737 cm^{-1} corresponding to ν(C=O) stretching vibration. A band at 1515 cm^{-1} represents the ν(C=C) stretching vibration of the phenolic rings of phenolphthalein. The FT-IR spectra are almost the same in the 1200–1000 cm^{-1} region. which suggests that there is no chemical interaction between the doped material and the polysiloxane monolithic matrix.

Polarized Light Optical Microscopy

To shed more light on the nature of the interaction between phenolphthalein and silica, two photographs were taken for the free silica and the immobilized phenolphthalein using the polarizing microscope as shown in Figure 6. As it can be seen from the photograph for the silica (Figure 6A), the particle size distribution is wide, whereas in the photograph of the immobilized phenolphthalein (0.005 M and 0.0005 M) Figure 6B and C, the particle size is almost

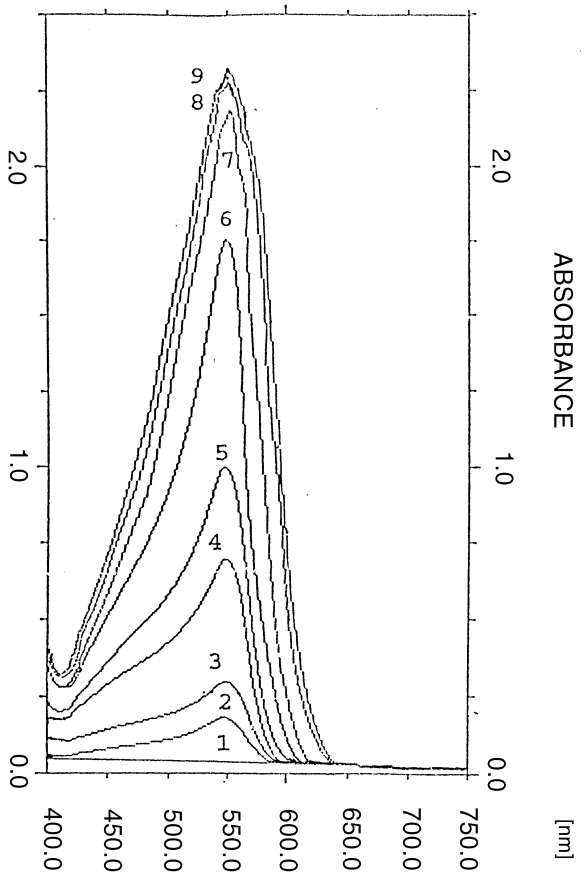

Figure 4. Electronic spectra of phenolphthalein (0.005 M) entrapped into silica matrix upon treatment with 0.10 M NaOH solution at different time intervals: 1—zero time (untreated sample), 2—after 1 minute, 3—after 2 minutes, 4—after 6 minutes, 5—after 9 minutes, 6—after 24 minutes, 7—after 45 minutes, 8—after 100 minutes, 9—after 120 minutes.

uniform and is relatively smaller than those of the silica obtained without entrapped phenolphthalein. This suggests that the loading of phenolphthalein into the silica matrix leads to smaller and more homogeneous particle sizes. This also has enlarged the exposure surface of the immobilized phenolphthalein.

Effect of Temperature

One of the most interesting aspect concerning this immobilized phenolphthalein is that, its color has changed into pink when heated to 100°C. It was also observed that the pink color of the sample has disappeared when it cools down to ambient temperature (23°C). This may suggest that at high temperature, the interaction of phenolphthalein leads to deprotonation of phenolphthalein and the basic form is obtained. At ambient temperature, the incorporated phenolphthalein is protonated probably from the environment (CO_2, H_2O) and therefore the acidic form appears. This was confirmed when the immobilized phenolphthalein is heated in vacuum under nitrogen, and cooled down to ambient temperature, the pink color was sustained.

Effect of Phenolphthalein Concentration

Different concentrations of trapped phenolphthalein were prepared and examined to obtain the optimum conditions at which the immobilized phenolphthalein shows high surface area and more sensitive to pH. From the results depicted in Figure 7 it is found that the best phenolphthalein concentration is 0.005 M, which gives maximum absorbance and highest surface area. This was confirmed from the UV/Vis spectra and the polarized microscope photographs. It is also possible to suggest that the phenolphthalein molecules be uniformly distributed within the silica network. It is found that there

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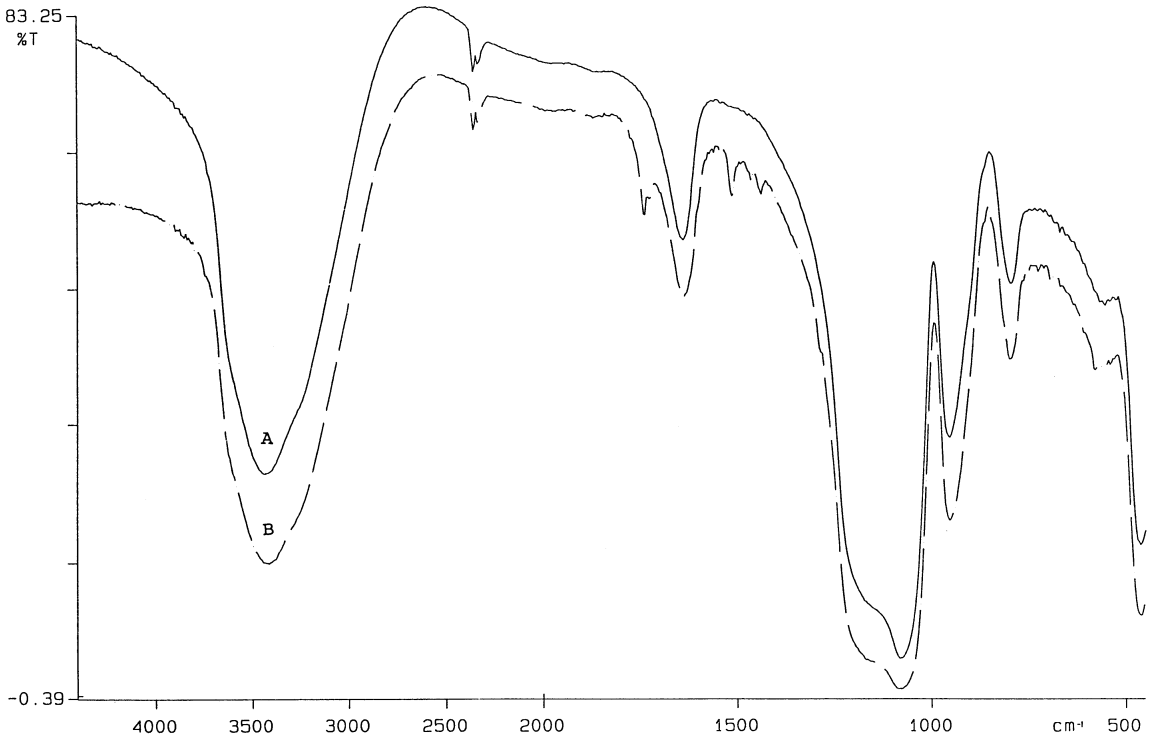

Figure 5. FT-IR spectra of: (A) free silica treated; (B) immobilized phenolphthalein.

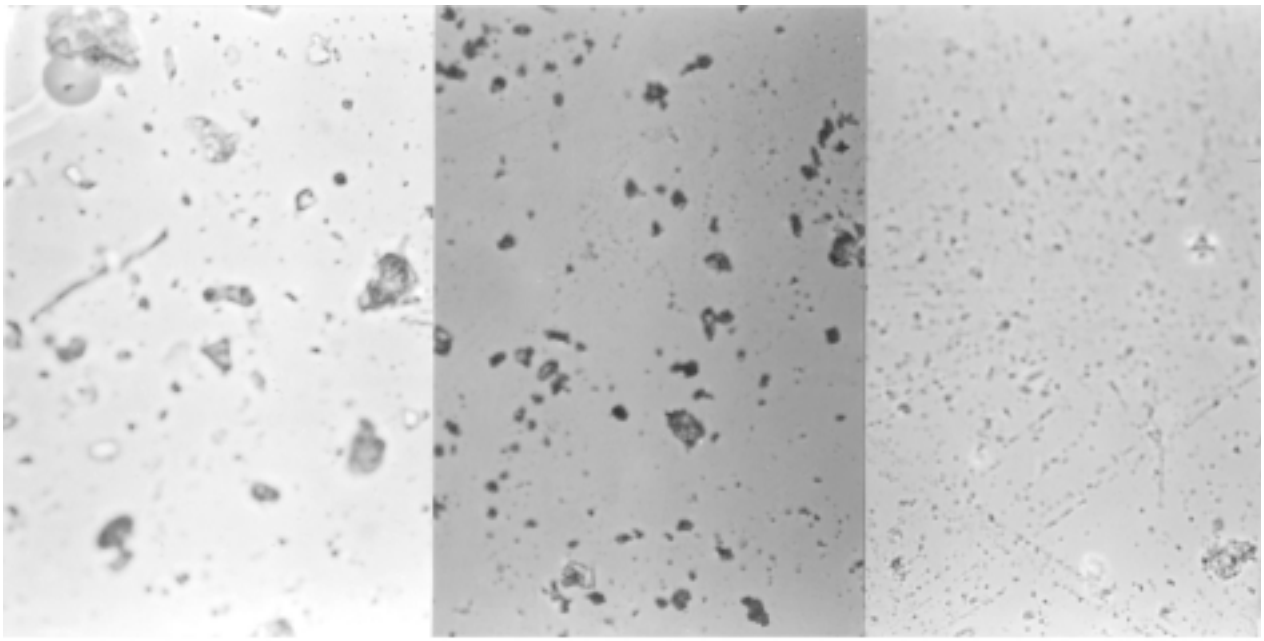

Figure 6. Cross-polarized microscope photographs: (A) free silica treated; (B) immobilized phenolphthalein, 0.0005 M; (C) immobilized phenolphthalein, 0.005 M.

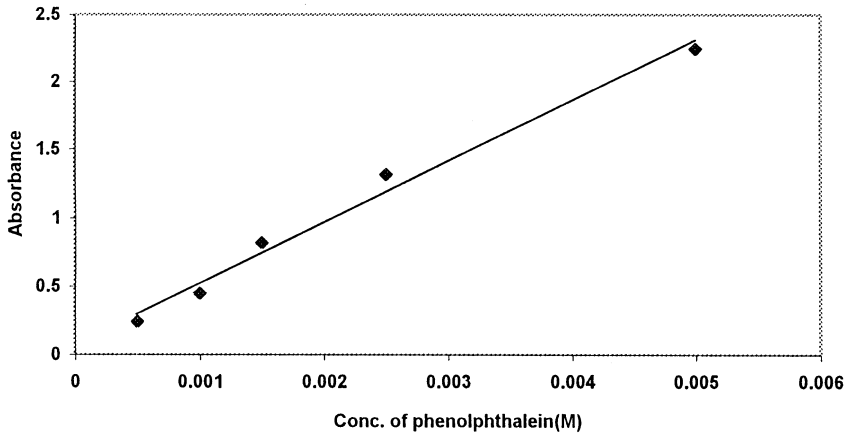

Figure 7. Absorption change of the hand at 553 nm versus the concentrations of entrapped phenolphthalein.

is a linear relation between the absorbance and the concentration of the entrapped phenolphthalein. This suggests that the phenolphthalein molecules have diffused homogeneously into the pores of the network of the silica.

Response to pH

The free phenolphthalein is present in different acid/base forms as a function of the pH of the solution. The phenolphthalein exhibits a pink color in basic solutions. When the phenolphthalein was trapped in SiO_2 solid support, the immobilized phenolphthalein exhibits the same change of color as it does in solution. This would give an advantage to using solid pH indicators.

CONCLUSION

This study shows that the phenolphthalein pH indicator can be doped into a sol-gel silica matrix and used for sensing pH. It is found that the immobilized solid indicator system is response to acid and base and can be used to monitor acid base reactions. The FT-IR and UV/Vis spectra showed weak interactions between the entrapped phenolphthalein molecules and the silica silanol groups. There is a uniform particle distribution within the silica network and smaller particle sizes for the immobilized phenolphthalein, in contrast with that of the free silica.

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